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IS 11255 (Part 5) (1990, Reaffirmed 2000): Methods for Measurement of Emission From Stationary Sources, Part 5: Total Fluoride. UDC 628.512 : 543.361.6



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IS 11255 (Part 5) : 1990

(Reaffirmed 1999)

भारतीय मानक

स्थिर स्रोतों से उत्सर्जन मापन की पद्धतियाँ

भाग 5 कुल फ्लोराइड

Indian Standard

REAFFIRMED

1 / Jan 2000

METHODS OF MEASUREMENT OF
EMISSIONS FROM STATIONARY SOURCES

PART 5 TOTAL FLUORIDE

(First Reprint NOVEMBER 2003)

UDC 628.512 : 543.361.6

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BUREAU OF INDIAN STANDARDS
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FOREWORD

This Indian Standard (Part 5) was adopted by the Bureau of Indian Standards on 15 March 1990, after the draft finalized by the Environmental Protection Sectional Committee had been approved by the Chemical Division Council.

Fluorine is one of the more common elements and occurs in at least trace amounts in virtually all natural and manufactured materials. Fluoride ion activity sensing electrode method is increasingly used nowadays for determination of total fluorides from stationary sources emission.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance, with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

*Indian Standard*METHODS OF MEASUREMENT OF
EMISSIONS FROM STATIONARY SOURCES

PART 5 TOTAL FLUORIDE

1 SCOPE

1.1 This standard (Part 5) prescribes a method for determination of total fluorides from emissions from stationary sources. It does not measure fluorocarbons, such as freons.

2 REFERENCES

2.1 The following Indian Standards are necessary adjuncts to this standard:

<i>IS No.</i>	<i>Title</i>
4167 : 1980	Glossary of terms relating to air pollution (<i>first revision</i>)
11255 (Part 1) : 1985	Methods of measurement of emissions from stationary sources: Part 1 Particulate matter

3 TERMINOLOGY

3.1 For the purpose of this standard the definitions given in IS 4167 : 1980 shall apply.

4 PRINCIPLE

4.1 Gaseous and particulate fluorides are withdrawn isokinetically from the source and collected in water and on a filter. The total fluoride is then determined by the specific ion electrode method.

5 RANGE AND SENSITIVITY

5.1 The range of this method is 0.020 to 2.000 $\mu\text{gF/ml}$; however measurements of less than 0.1 $\mu\text{gF/ml}$ require extra care.

6 INTERFERENCES

6.1 Grease on exposed surfaces may cause low fluoride results because of absorption.

7 APPARATUS**7.1 Sampling Train**

The sampling train shall be same as for particulate matter determination. See IS 11255 (Part 1) : 1985

7.2 Distillation Apparatus

The apparatus shall be of glass and shall be assembled as shown in Fig. 1.

7.3 Bunsen Burner

7.4 Electric Muffle Furnace, capable of heating to 600°C.

7.5 Crucibles Nickel, 75 to 100 ml.

7.6 Beakers, 500 ml and 1500 ml.

7.7 Volumetric Flasks, 50 ml.

7.8 Erlenmeyer Flasks or Polyethylene Bottles

7.9 Constant Temperature Bath

Constant temperature bath shall be capable of maintaining a constant temperature $\pm 1.0^\circ\text{C}$ at room temperature conditions.

7.10 Fluoride-ion Activity Sensing Electrode, suitable.

7.11 Reference Electrode, single function, sleeve type.

7.12 Electrometer

Electrometer shall have a pH meter with mV scale, capable of 0.1 mV revolution or a specific ion meter made specifically for specific ion use.

7.13 Magnetic Stirrer and Fluorocarbon Coated Stirring Bars

8 REAGENTS

8.1 Calcium Oxide, containing 0.005 percent F or less.

8.2 Phenolphthalein Indicator (0.1 percent)

Dissolve 0.1 g of solid phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml of deionized distilled water.

8.3 Sodium Hydroxide, pellets.

8.4 Sulphuric Acid, concentrated.

8.4.1 Sulphuric Acid, 25 percent (v/v)

Prepare by mixing 1 part of concentrated sulphuric acid with 3 parts of deionized distilled water.

8.5 Filters

8.5.1 Whatman No. 541 or equivalent. The filters

are required for filtration of impinger contents and preparation of sample for analysis.

8.6 Sodium Hydroxide Solution, 5 M

8.6.1 Prepare by dissolving 20 g of sodium hydroxide in 100 ml of deionized distilled water.

8.7 Total Ionic Strength Adjustment Buffer (TISAB)

8.7.1 Place 500 ml of double distilled water in a 1 litre beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride and 0.30 g of sodium citrate. Stir to dissolve. Place beaker in a water bath (for cooling) and slowly add 5 M sodium hydroxide until the pH is between 5.0 to 5.5. Cool to room temperature and pour into a 1 litre volumetric flask and make it up to mark with double distilled water.

8.8 Standard Fluoride Solution, 0.1 M

Prepare by dissolving 4.2 g of oven dried (at 110°C) sodium fluoride in 1 litre of double distilled water in a volumetric flask.

9 PROCEDURE

9.0 Sampling, sample recovery, sample preparation and distillation shall be as follows.

9.1 Preparation of Collection Train

9.1.1 Preparation of collection train is same as for particulate matter determination [see IS 11255 (Part 1) : 1985] except for the following variation. Place 100 ml deionized distilled water in each of the first two impingers and leave the third impinger empty. Transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the fourth impinger. Assemble the train as shown in Fig. 1 with the filter between third and fourth impingers.

9.2 Sample Recovery

9.2.1 The probe is removed from stack and properly cleaned up externally. Allow the probe to cool till it is safely handled. Wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent from losing part of the sample. Transfer the train to a clean site, remove the probe from sampling train, wipe off silicon grease. Remove the umbilical cord from the last impinger and cap the impingers. Transfer the probe and filter impingers assembly to an area that is clean and protected from wind to avoid chances of contamination. Treat the sample as follows:

Container No. 1

(Probe, filter and impinger catches). The volume of the water in the first impinger is recorded using

a graduated cylinder (measure to the nearest millilitre). Include any condensate in the probe in this determination. Transfer the impinger water from the graduated cylinder into the polyethylene container. Add the filter to this container taking care that dust on the outside of the probe or other exterior surface does not get into the sample. Clean all sample exposed surfaces (including the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors and filter holder) with deionized distilled water. Use less than 500 ml for the entire wash. Add the washings to the sampler container. Perform the deionized distilled water rinses as follows:

Carefully remove the probe nozzle and rinse the inside surface with deionized water from a wash bottle. Brush with a nylon bristle brush and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the fitting with deionized distilled water in a similar way.

Rinse the probe liner with deionized distilled water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surface will be wetted with water. Let the water drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring the liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position and squirt deionized distilled water into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With a stainless steel or other metal probe, run the brush through, in the above prescribed manner at least six times, since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with deionized distilled water, and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above. It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Rinse the inside surface of each of the first three impingers (and connecting glassware) thrice separately. Use a small portion of deionized distilled water for each rinse, and brush each sample-exposed surface with a nylon bristle brush, to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush.

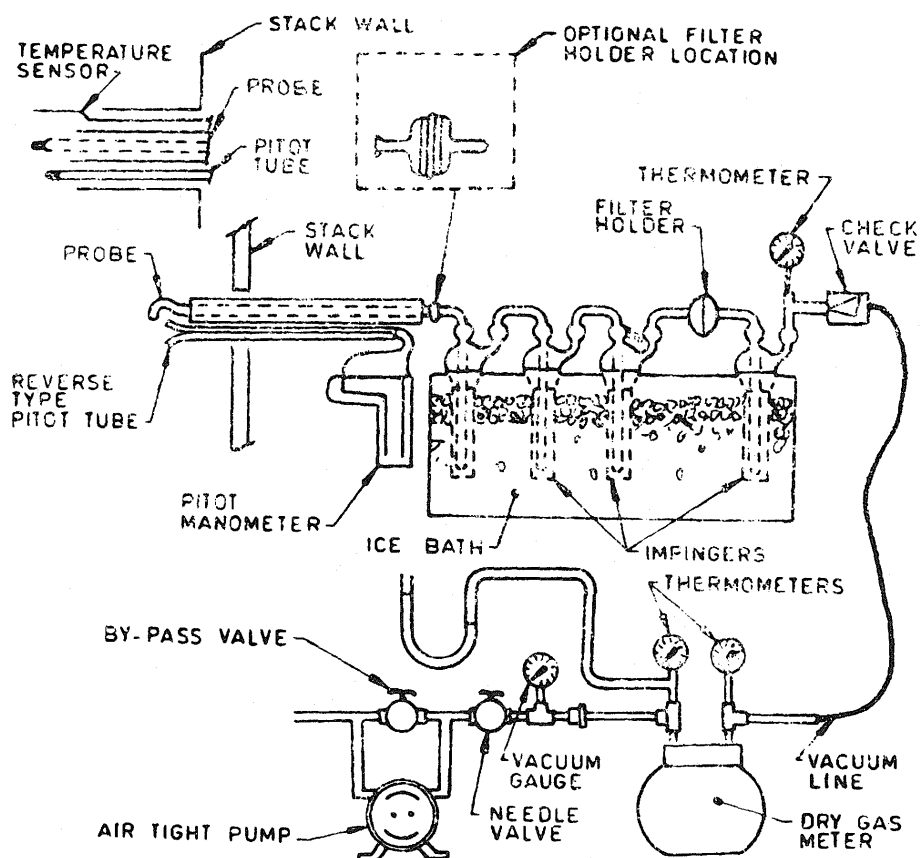


FIG. 1 FLUORIDE SAMPLING TRAIN

After ensuring that all joints have been wiped clean of the silicone grease, brush and rinse with deionized distilled water the inside of the filter holder (front-half only, if filter is positioned between the third and fourth impingers). Brush and rinse each surface thrice or more, if needed. Make a final rinse of the brush and filter holder.

After all water washings and particulate matter have been collected in the sampler container, tighten the lid so that water will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container clearly to identify its contents.

Container No. 2 (Sample Blank)

Prepare a blank by placing an unused filter in polyethylene container and adding a volume of water equal to the total volume in container No. 1. Process the blank in the same manner as for container No. 1.

9.3 Sample Preparation

9.3.1 Treat the contents of each sample container

as described below:

Container No. 1

(Probe, filter and impinger catches.) Filter the contents of the container including the sampling filter, through Whatman No. 541 or equivalent filter paper into a 1 500 ml beaker. If filtrate volume exceeds 900 ml, make the filtrate basic (red to phenolphthalein) with NaOH and evaporate to less than 900 ml. Place the filtered material (including sampling filter) in a nickel crucible, add a few ml of deionized distilled water and macerate the filters with a glass rod. Add 100 mg of calcium oxide to the crucible and mix the contents thoroughly to form a slurry. Add two drops of phenolphthalein indicator. Place the crucible on hot plate at low heat till the water completely evaporated. The slurry to be kept basic (red to phenolphthalein) to avoid loss of fluoride. If the indicator turns colourless (acidic) during the evaporation, add calcium oxide until the colour turns red again.

After evaporation of water, place the crucible on hot plate and slowly increase the temperature until the Whatman filter paper chars. Place the crucible in a cold muffle furnace, increase the

temperature gradually to 600°C until the contents are reduced to ash. Remove crucible from furnace and allow to cool. Add approximately 4 g of crushed sodium hydroxide to crucible and mix. Return the crucible to muffle furnace and fuse the sample for 10 minutes at 600°C. Remove the sample from the furnace and cool to ambient temperature. Using several rinsing of warm deionized distilled water, transfer the contents of crucible to the beaker containing the filtrate. To assure complete sample removal rinse finally with two 20 ml portion of 25 percent sulphuric acid and carefully add to the beaker. Mix well and transfer to 1 litre volumetric flask. Dilute to volume with deionized distilled water, mix thoroughly and allow undissolved solids to settle. Container No. 2 (Sample Blank).

Process the sample in the same manner as per container No. 1.

Adjustment of acid water ratio in distillation flask

Place 400 ml of deionized distilled water in distillation flask and 200 ml of concentrated sulphuric acid slowly with swirling add some soft glass beads and assemble the apparatus as shown in Fig. 2. Heat the flask until the temperature

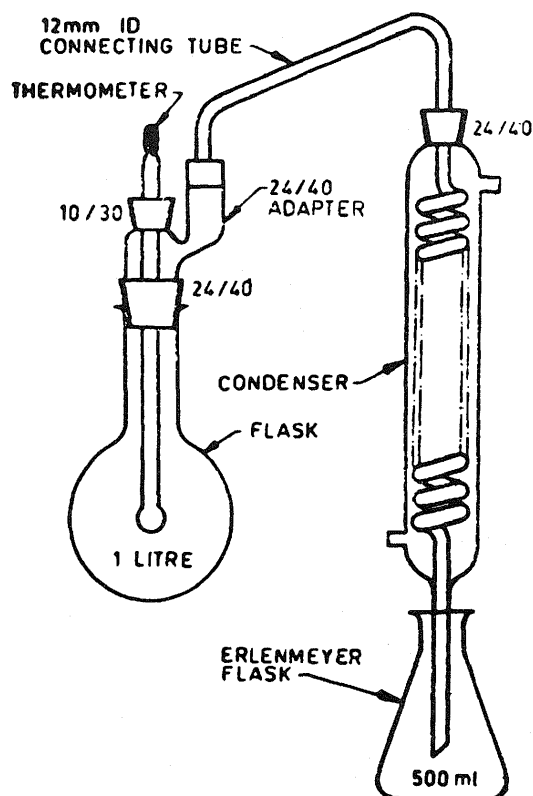


FIG. 2 FLUORIDE DISTILLATION APPARATUS -

reaches 175°C to adjust acid water ratio for subsequent distillations. Discard the distillate.

9.4 Distillation

9.4.1 Cool the content of the distillation flask to above 80°C. Pipette an aliquot of sample containing less than 10.0 mg F directly into the distillation flask and add deionized distilled water to make total volume of 220 ml. Place 250 ml volumetric flask at condenser exit. Heat the flask as rapidly as possible with Bunsen burner. Collect all distillate up to 175°C. (Temperature not to be exceeded 175°C, otherwise sulphuric acid will distil over). Conduct the distillation within 15 minutes or less. Slow distillation have been found to produce low fluoride recoveries. The acid in the distillation flask may be used until there is carry over to interferences or poor fluoride recovery. Change the acid whenever the fluoride recovery is less than 90 percent or the blank value exceeds 0.1 µg/ml.

9.5 Analysis

9.5.1 Containers No. 1 and 2

After distilling suitable aliquots from containers No. 1 and 2, dilute the distillate in the volumetric flask to exactly 250 ml with deionized distilled water and mix thoroughly. Pipette 25 ml of aliquot from each of the distillate into separate beakers. Add an equal volume of TISAB and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than $\pm 2^\circ\text{C}$ from the temperature at which the calibration standards were measured, condition samples and standards in a constant temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution temperature, place a piece of temperature insulating material such as cork, between the stirrer and the beaker. Hold dilute samples (below 0.000 4 M fluoride ion content) in polyethylene beakers during measurement.

Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with deionized distilled water.

9.6 Calibration

Maintain a laboratory log of all calibrations.

9.6.1 Fluoride Electrode

Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipette 10 ml of 0.1 M fluoride standard solution

into a 100 ml volumetric flask and make up to the mark with deionized distilled water for a 10^{-2} M standard solution. Use 10 ml of 10^{-2} M solution to make a 10^{-3} M solution in the same manner. Repeat the dilution procedure and make 10^{-4} M and 10^{-5} M solutions. Pipette 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. Stir the solution with magnetic stirrer when a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, that is when 50 ml of 10^{-2} M standard is diluted with 50 ml of TISAB the concentration is still designated ' 10^{-2} M'.

Between measurements soak the fluoride sensing electrode in deionized distilled water for 30 seconds, and then remove and blot dry. Analyze the standards, going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} and 10^{-1} fluoride molarity on the log axis plotted versus electrode potential (in mV) on the linear scale. Some electrodes may be slightly nonlinear between 10^{-5} M and 10^{-4} M. If this occurs, use additional standards between these two concentrations.

Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10^{-3} M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.

NOTE — Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of the fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride.

10 CALCULATIONS

10.1 Total Fluoride in Sample

Calculate the amount of total fluoride in the sample using the following equation:

$$F_t = \frac{V_t}{A_t} (V_d) (M)$$

where

M = concentration of F from calibration curve, molarity.

V_t = total volume of F in sample, after final dilution, ml.

A_t = aliquot of total sample added to still, ml.

V_d = volume of distillate as diluted, ml.

F_t = total F in sample, mg.

10.2 Fluoride Concentration in Stack Gas

Determine the fluoride concentration in the stack gas, C_s , using the following equation:

$$C_s = \frac{F_t}{V_m (\text{std})}$$

where

$V_m (\text{std})$ = volume of gas sample as measured by dry gas meter, corrected to standard conditions.

